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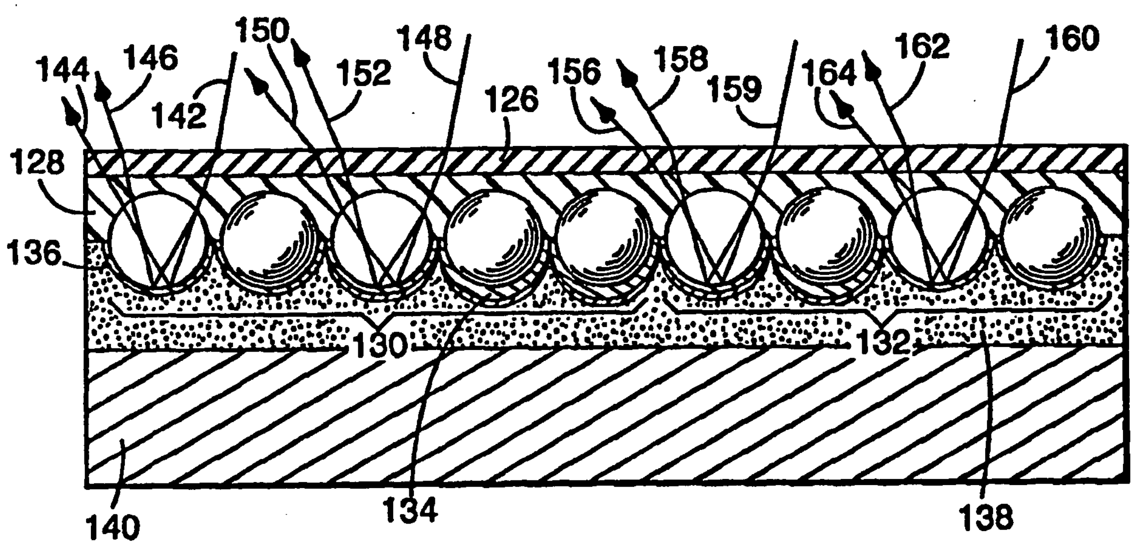

(57) Abstract

This invention relates to graphic films which exhibit a rainbow-like color image visible at certain conditions of illumination and observation, but, additionally expands the range of visual effects to produce very subtle hidden images, or 3-dimensional appearing images, or more dramatic images which change from photographic positive to a photographic negative or vice-versa as the viewing angle is changed relative to the illumination source.

RAINBOW SHEETING HAVING DISTINCT COLOR CHANGES AND/OR HIDDEN IMAGES

Field of the Invention

This invention relates to graphic films which exhibits a rainbow-like color image visible at certain conditions of illumination and observation, but, additionally expands the range of visual effects to produce very subtle hidden images, or 3-dimensional images, or more dramatic images which change from photographic positive to a photographic negative or vice-versa as the viewing angle is changed relative to the illumination source.

Background of the Invention

"Rainbow" film, is a decorative variation of enclosed lens retroreflective sheeting known by those skilled in the art of retroreflective optics. Fig. 1 illustrates a known rainbow film construction. This film has laminated and/or coated layers of, in order from the surface, a transparent surface film 2, a glass microsphere bonding layer 4, high refractive index glass microspheres 6, a metal reflective coating 8, an adhesive layer 10 for attaching to a substrate, and a release sheet 12 for protecting the adhesive until it is applied to the substrate. The back side of the glass microsphere bonding layer 4 holds the glass microspheres in a roughly half-embedded state. Also, the metal reflecting coat conforms to the non-embedded backside of the glass microspheres, such that, incident visible light rays entering the front side of the sheet and glass microsphere are dispersed into their spectral components. Thus a rainbow is observed off angle from a point light source. The rainbow is not visible under all conditions of illumination. For example, with a commercial film sold by Sumitomo/3M called Scotchlite™ Rainbow film the viewer must be positioned between 27-42 degrees off axis from an illumination source like the sun or a spotlight to observe the dispersed colors. Rainbow film has been used as a decorative film for displays or decals whereby the film is cut into an image and affixed to a substrate. It has also been supplied in colors wherein a transparent pigment is dispersed in the surface layer. This construction changes color at the angles where the reflected dispersion color is visible

by mixing with the rainbow colors. Rainbow film has also been surface printed with opaque inks to provide colored images contrasting with the viewing angle dependent rainbow colors. Additionally, it has been surface printed with images in transparent colored inks which appear to change color due to the influence of the viewing angle dependent rainbow color change underneath. None of these films possess a coating in the form of an image on some of the microspheres which is formed in between the microsphere surface and the reflective coating surface. Additionally, the known graphic films do not use microspheres having different refractive index averages in more than one section of the sheeting. Furthermore, they do not use more than one transparent bonding layer having different refractive indices in more than one section of the sheeting.

Summary of the Invention

The present invention expands the range of visual effects previously available with "Rainbow" film to create new images ranging from the very subtle to dramatic effects. The present invention provides a "Rainbow" graphic film with capability for creating enhanced visual effects with a wider viewing range and more sophisticated images including pseudo 3-dimensional images. Further, with this invention it is possible to create large area spectral displays which exhibit a uniform and gradual rainbow-like color change, or more than one rainbow-like color change at different viewing angles relative to an illuminating source.

Furthermore, by adjusting the design parameters of this invention it is possible to provide hidden images within the boundaries of the original design that appear and disappear depending on the viewing angle, or create the illusion of a 3-dimensional appearance.

The present invention provides a first graphic film comprising:

(a) a layer of transparent solid glass microspheres bonded to a transparent microsphere bonding layer, wherein the microspheres are partially embedded in the transparent microsphere bonding layer, wherein about 20% to about 80% of the average diameter of each microsphere is embedded in the transparent microsphere bonding layer, and wherein the ratio of the transparent microsphere refractive index to

the transparent microsphere bonding layer refractive index is about 1.3:1 to about 1.7:1;

(b) at least one non-reflective coating in the form of an image on some of the microspheres wherein said coating(s) is on surface(s) of the microspheres not embedded in the transparent microsphere bonding layer;

(c) a reflective coating coated on the surfaces of the microspheres not embedded in the transparent microsphere bonding layer, wherein for the microspheres coated with the non-reflective coating(s) of element (b), the reflective coating is coated over the non-reflective coating(s) of element (b);

(d) an optional adhesive layer affixed on the side of the reflective coating opposite the microsphere layer;

(e) an optional transparent release liner affixed to the adhesive layer, when present; and

(f) an optional transparent film affixed to the transparent microsphere bonding layer opposite the side in which the layer of transparent solid glass microspheres is embedded.

The coating of element (b) may be in the form of an image, such as lettering, scrolls, or decoration, etc. The graphic film typically comprises a monolayer of transparent glass microspheres having a typical average diameter of between about 40-150 microns, the microsphere image being embedded in a transparent microsphere bonding layer such that about 20% to about 80% of the average microsphere diameter is not embedded in the bonding layer.

One aspect of this invention relates to a graphic film wherein a portion of the transparent microspheres have a transparent coating of varying thickness printed thereon so that the thickness of the coating on some of the glass microspheres is different than the coating on other microspheres so that some of the image has a subtle watermark character while another portion has a more of a retroreflective character. This could be used to create the illusion of depth or 3-dimensionality, since the observed shift in dispersed color varies from one portion of the image to another as a function of viewing angle. The coating thickness variation could be gradual, as in the printing of a graded halftone, diffusion dither or stochastic dither pattern, or stepwise

as in overprinting one image with another to create different visual effects, such as a drop shadow.

A further aspect of this invention is to vary the refractive index of the transparent glass microsphere bonding layer so that at least one section of the rainbow film has a different reflected dispersion angle.

A further embodiment of this invention involves variations within the aforesaid design parameters to create more visually complex images. Examples of such variation include but are not limited to providing more than one microsphere refractive index population, and/or more than one transparent microsphere bonding layer refractive index, within a given image area to create additional visual contrast between adjacent elements of the image.

As mentioned above, one or more coatings such as an ink is provided on the second surface side of the monolayer of transparent microspheres (the side not embedded in the transparent microsphere bonding layer) to further alter the optical path. These coating(s) may be in the form of images. If the coating is transparent and thin, it will shift the viewing angle of the refracted colored image away from the light source, creating a contrasting image to the refracted color in the adjacent unprinted area. Since each transparent glass microsphere embedded in the microsphere bonding layer acts as a catadioptric lens which converges the light rays entering through the transparent substrate, it is possible to control the thickness of the one or more transparent coating(s) on the exposed surface of some of the glass microspheres to achieve the focal point of the lens wherein the yellow portion of the spectrum is converged on the back surface of the coating(s). This appears to act as an achromatic doublet lens to reverse the chromatic aberration caused by the dispersion of the light in the microsphere. If a transparent and colorless coating(s) is used of sufficient thickness and refractive index to achieve this lens focal point, a retroreflected image results which is brighter than the uncoated microspheres when the viewing angles are less than the range where the prismatic display may be observed (nearer the light source). At the same time, this image appears darker than the unprinted background at the viewing angles where the prismatic display may be observed. At viewing angles greater than the viewing range of the prismatic display, the coated and uncoated

microspheres appear almost the same, meaning the image largely disappears. If the coating thickness is increased beyond this lens focal point on some of the microspheres, the color dispersion effect is negated and the color of the reflective coating is seen at all viewing angles, in contrast with the uncoated microspheres. Finally, because of the angular dependence of these images on coating thickness, it is possible to create an illusion of depth or 3-dimensionality, by proper choice of image and image position, i.e., such as by use of a drop shadow.

The present invention also provides a second graphic film comprising:

(a) a layer of transparent solid glass microspheres partially embedded in a transparent microsphere bonding layer, wherein about 20% to about 80% of the average of each microsphere diameter is embedded in the transparent microsphere bonding layer, wherein the ratio of the transparent microsphere refractive index to the transparent microsphere bonding layer refractive index is about 1.3:1 to about 1.7:1;

(b) a reflective coating coated on the surfaces of the microspheres not embedded in the bonding layer;

(c) an optional adhesive layer affixed on the side of the reflective coating opposite the transparent microsphere bonding layer; and

(d) an optional release liner affixed to the adhesive layer, when present;

(e) an optional transparent film affixed to the transparent microsphere bonding layer opposite the side in which the layer of transparent solid glass microspheres is embedded;

wherein one or both of the following are true:

(i) wherein the layer of transparent solid glass microspheres has at least two sections wherein the microsphere refractive index averages differ by at least 0.01;

(ii) wherein the transparent microsphere bonding layer has at least two adjacent sections wherein the transparent microsphere bonding layer refractive indices differ by at least 0.01.

The second graphic film may optionally further comprise at least one coating on some of the microsphere surfaces not embedded in the bonding layer.

Within the scope of the invention is envisioned the use of pressure sensitive adhesives, heat activated adhesives, or solvent activated adhesives, for affixing the graphic films of the invention to a substrate. Also primer layers may be used in between the optional adhesive layer and the reflective coating and/or between the microsphere bonding layer and the optional transparent film.

Preferred non-reflective coatings useful in the present invention are selected from the group consisting of inks, paints, lacquers, and varnishes.

Definition of Terms

The term "retroreflection" as used herein refers to the property wherein radiation is returned in, or close to, the direction from which it came, this property being maintained over wide variations in the direction of the incident radiation.

The term "reflective" as used herein in reference to coatings refers to coatings which if formed on a smooth, flat surface, such as a glass slide, would specularly reflect at least 85% of the incident white light falling thereon.

The term "non-reflective" as used herein in reference to coatings refers to coatings which if formed on a smooth flat surface such as a glass slide, would specularly reflect less than 85% of the incident white light falling thereon.

The term "transparent" as used herein refers to a material wherein the ratio of the intensity of undeviated light passing through a bulk layer to the incident light is equal to or greater than about 85%.

The term "opaque" as used herein refers to a material wherein the ratio of the intensity of undeviated light passing through a bulk layer to the incident light is equal to or less than about 20%.

The term "lens focal point" as used herein refers to the condition whereby the yellow portion of the spectrum of the incident white light transmitted through the graphic film is converged to the reflective coating by the catadioptric lens system created by the glass microspheres having one or more transparent coatings formed thereon, and embedded in the microsphere bonding layer, to result in a contrasting image visible near the light source.

The term "formed" as used herein includes the terms "coated," "extruded," "transfer coated," "laminated," etc.

Brief Description of the Drawings

Fig. 1 is a cross-section of a prismatic graphic film of the prior art.

Fig. 2 is a cross-section of a prismatic graphic film of the invention.

Figs. 3-6 are cross-sections of other embodiments of prismatic graphic films of the invention.

Fig. 7 is a representation of a viewing condition of a prismatic graphic film of the invention.

Fig. 8 is a plan view of a 3-dimensional appearing embodiment of a prismatic film of the invention.

Fig. 9 is a cross-section of a graphic film of the invention taken along line 9-9 of Fig. 8.

Detailed Description of the Invention

Transparent Glass Microspheres

The transparent glass microspheres used in the articles of the invention are preferably colorless. Transparent colored or slightly colored microspheres may be useful but they would tend to filter out certain colors. The transparent microspheres must be solid rather than hollow. The microspheres are preferably free from flaws and imperfections. Due to processing difficulties, the microspheres may possess some minor flaws such as phase separation, crystallinity and haziness. The greater the number of microspheres containing flaws the lower the color intensity of the prismatic display. It is also possible that a small number of hollow microspheres may be produced along with the solid microspheres due to processing difficulties. The article could still be prepared without separating out the minor amount of hollow microspheres. However, these hollow microspheres would not contribute to the prismatic display.

The diameters of the transparent microspheres can vary. Typically, the average diameter of the transparent microspheres ranges from about 40 to about 150 microns,

and preferably about 60 to about 90 microns. As the average diameter of the microspheres is reduced below about 60 microns, diffractive effects can occur which tend to reduce the saturation of color (i.e., a milky color results.) If the average diameter of the microspheres is greater than about 140 microns, the microspheres become more visible to the naked eye, thus providing a grainy appearance. In addition, the prismatic display appears somewhat less continuous with increase in microsphere diameter. Also, larger microspheres tend to be less cost effective as they cover less area on a weight basis and can require a greater amount of bonding material to adhere the layers together. Typically, microspheres are used which differ in diameter by not more than about 60 microns, preferably not more than about 30 microns, and most preferably not more than about 20 microns, in order to obtain a more uniform appearing graphic film and a prismatic display having vibrant colors.

The refractive indices of the transparent microspheres can vary as long as the ratio of the refractive index of the microspheres to the refractive index of the transparent bonding layer falls within the indicated range. The refractive index of the microspheres is typically at least about 1.93 for availability reasons of the microsphere bonding layer, more typically about 2.1 to about 2.3.

When microspheres having more than one refractive index average are used in two or more different sections of the graphic film, a visible color contrast resulting in an image can be seen in as little as 0.01 refractive index difference. Preferably the difference is greater than 0.03. The larger the refractive index difference, the greater the viewing angle separation of the prismatic display. If the refractive index difference is about 0.15 - 0.20 or greater difference, the rainbow approaches a non-overlapping state, i.e., the progression of violet to red or red to violet is repeated as one changes the viewing angle relative to a light source.

The transparent microspheres may be treated with adhesion promoters such as silanes, titanates, chromates or the like to improve adhesion to the transparent bonding layer. They may also be treated with surface energy lowering coatings such as silicones or fluorocarbons to help control the embedment process.

Transparent Microsphere Bonding Layer

The transparent microsphere bonding layer should be capable of adhering to the microspheres and to the optional transparent film if present, such that the surface of the graphic film of the invention can be cleaned without debonding. The bonding layer is preferably insoluble in or, unaffected by normal cleaning materials such as water, alcohol, surfactants, etc. The microsphere bonding layer preferably is capable of adhering to the microspheres and the optional transparent film over a fairly wide temperature range (i.e., about -45°C to about 70°C). The microsphere bonding layer should be capable of being processed such that the microspheres can be embedded to the proper depth. Typically, the bonding material is either soluble or dispersible in a solvent from which it can be cast, or is capable of being cast via thermoplastic extrusion. The transparent bonding layer is typically colorless but may be colored, depending on the decorative affect desired.

The transparent microsphere bonding layer can comprise a number of different materials. The bonding material may be solvent-based, water-based or a 100% solids resin. The bonding layer may be, for example, a thermoplastic or thermosetting material. Crosslinked materials generally provide better solvent resistance, humidity resistance, and temperature stability. Preferably the transparent microsphere bonding layer is weather resistant so the graphic film may be affixed to an exterior surface. If not, the optional transparent film layer is preferably weatherable. A primer may be used in between the microsphere bonding layer and the optional transparent film.

Suitable bonding materials include but are not limited to those selected from the group consisting of polyurethanes; acrylic polymers and copolymers such as polymethyl methacrylate, etc.; modified acrylic polymers and copolymers such as polyethylene acrylic acid, polyethylene methacrylic acid and its metal salt modified polymers; polyesters such as polyvinyl acetate, etc.; polycarbonates; epoxies; polyethers; vinyl copolymers; melamine polyesters; modified melamine polyesters such as butylated melamine polyesters, etc.; fluoropolymers; blends thereof, etc. Preferably the transparent bonding layer is selected from the group consisting of polyethylene methacrylic acid copolymers modified with zinc, melamine modified polyesters, acrylic

polymers and copolymers, polyurethanes, and blends thereof (for weatherability and processing reasons).

The refractive index of the bonding layer can vary as long as the ratio of the transparent microsphere refractive index to the transparent bonding layer refractive index is about 1.3:1 to about 1.7:1. This ratio is important because it determines where a viewer will observe the prismatic display. For one to observe the prismatic display a source of light must illuminate the microsphere containing film. The geometric orientation of the illumination source, article and viewer is important in designing the visual decorative effects of the article of the invention. For definition purposes geometric conventions similar to those used in the art of retroreflective optics are followed herein. These can be found in the Commission Internationale de l'Èclairage (CIE) Publication 54 and in ASTM standard E-808. Herein, the term "retroreflector" used within the CIE convention has been replaced with the term "substrate", meaning the substrate on which the graphic film of the invention is applied. A brief synopsis of the important definitions used herein are as follows: Referring to Fig. 7, the substrate center 278 is a point on a substrate 260 which is designated to be the center of the device for the purpose of specifying its performance. The illumination axis 270 is defined as a line segment from the substrate center 278 to the source of illumination 266. The observation axis 268 is defined as a line segment between the substrate center 278 to the observer 264. The substrate axis 274 is a perpendicular line segment from the substrate center 278 which is used to define the angular position of the substrate 260. The entrance angle 276 (also herein referred to as the illumination angle) is the angle from the illumination axis 270 to the substrate axis 274. The observation angle 272 (also referred to herein as the viewer or viewing angle) is the angle between the illumination axis 270 and the observation axis 268.

The light emitted by the illumination source passes, in sequence, through the optional transparent film, the transparent microsphere bonding layer, the microspheres, and the coating, where present. The microspheres disperse the light into the visible spectrum and a portion of it is refracted back by the reflective coating at an angle different from the illumination angle, where it may be observed. It has been discovered that for any given ratio of microsphere refractive index to microsphere bonding layer

index within the aforesaid limits, a prismatic display is visible in a radially symmetric cone segment or annular viewing ring which is about 15-20 observation angle degrees wide, when the illumination angle is fixed at 0 degrees. This is believed to be due to the spherical nature of the microspheres. The lower angle within any given viewing ring corresponds to the shorter wavelength violet color of the spectrum and the higher angle to the higher wavelength red color of the spectrum, with the remaining spectral colors observed between the limits. To study this effect, a series of varying reference refractive index liquids were smeared on a transparent biaxially oriented PET film and sprinkled with beads of varying refractive index. When viewed from the PET side with a light source, this method appears to closely approximate a microsphere layer embedded in a bonding layer and coated with a reflective coating. At the lower aforesaid ratio of 1.3:1 the annular viewing ring approaches 90 degrees observation angle and therefore is a lower practical limit. The higher aforesaid ratio of 1.7:1 defines an annular viewing ring that approaches 0 degrees observation angle and is therefore an upper practical limit. This effect does not appear to be linear, i.e., higher refractive index microspheres have slightly higher ratios for a given viewing angle range. The preferred range of the aforesaid ratio is between about 1.35-1.55, which corresponds to observation angles of the red color of the spectrum from about 65-25 degrees respectively. The following table provides information which allows one to choose the refractive indices of the microsphere bonding layer and/or microspheres to help design a starting point to define the angular range where the prismatic display is observed.

Microsphere R.I. / Reference Liquid R.I.	Ratio	Observed Angle of Color*				
		Violet	Blue	Green	Yellow	Red
1.93/1.400	1.38	39	44	49	52	59
1.93/1.448	1.33	55	60/1	64	68	72
1.93/1.496	1.29	No Spectrum Observed				
2.10/1.400	1.50	14	18	22	25	30/31
2.10/1.448	1.45	22	26	30	33	38/39
2.10/1.496	1.40	30	34	38/39	41/42	48
2.10/1.516	1.38	35	39	44/45	47/48	52/53

Microsphere R.I. / Reference Liquid R.I.	Ratio	Observed Angle of Color*				
		Violet	Blue	Green	Yellow	Red
2.10/1.544	1.36	42/3	46/7	51	54/55	60
2.10/1.592	1.32	56	61	66	71	N.O.
2.10/1.640	1.28	No Spectrum Observed				
2.19/1.400	1.56	10	15	20	23	26/27
2.19/1.448	1.51	19	24	28/29	30/31	35
2.19/1.496	1.46	28	32	36/37	39/40	45
2.19/1.516	1.44	31	35	41/42	45	49
2.19/1.544	1.42	41/42	45/46	49	52/53	56
2.19/1.592	1.38	55	60	65/66	68	71
2.19/1.644	1.33	No Spectrum Observed				
2.26/1.400	1.61	7/8	11	16/17	18/19	21/22
2.26/1.448	1.56	16/7	19/20	22/23	24/25	28
2.26/1.496	1.51	22	26	29/30	32/33	36
2.26/1.516	1.49	26	30	34	36/37	39
2.26/1.544	1.46	33	35/46	39	42/43	44/45
2.26/1.592	1.42	42	46/47	50	53/54	57
2.26/1.644	1.38	58	61	66	71	75/76
2.26/1.692	1.33	No Spectrum Observed				
2.60**/1.40	1.86	N.O.	N.O.	N.O.	N.O.	N.O.
260**/1.448	1.80	N.O.	N.O.	N.O.	N.O.	N.O.
2.60**/1.495	1.73	N.O.	N.O.	3/4	7	11
2.60**/1.516	1.71	N.O.	0-2	5/6	9	13
2.60**/1.544	1.68	N.O.	0-5	8/9	11/12	15
2.60**/1.592	1.63	5	11	15/16	19	21
2.60**/1.644	1.58	10	14	17/18	21	23/24
2.60**/1.692	1.54	16/17	21/22	25	28	30

N.O. = No Color Observed
R.I. = Refractive Index
* In degrees
** The available transparent microsphere for this range of refractive index was yellow in color so the stated angles are approximations only.

When a viewer is standing within the viewing ring for a single combination of the aforesaid refractive indices the portion of the spectrum that the viewer sees, and the relative position of the colors (if more than one color is visible at the same time) is dependent on the area of illumination, the size of the area containing the aforesaid microsphere containing graphic film within the area of illumination and the relative distance of the viewer and the light source from the graphic film to define the aforesaid observation angle range.

A method of defining what the viewer will see from a given position is as follows: Draw a two-dimensional diagram of the viewing situation using proportional spacing for the graphic film width, the illumination width (if smaller than the width of the microsphere image), the illumination source position and distance, and the viewer position and distance. Draw two line segments from the center of the light source to the edges of the illuminated portion of the graphic film affixed to the substrate, closest to the viewer and furthest from the viewer. Next, draw two line segments from each of these points to the viewer's eye. Measure each of these observation angle limits. Compare these angles to the aforesaid table for a similar refractive index ratio combination. If both angles are within the range of the prismatic viewing ring the lower of the two measured angles will approximate the shortest wavelength color of the spectrum (violet side) that the viewer will see from that position, while the higher will determine the longest wavelength color.

If the source of illumination is very much further away from the graphic film display surface than the viewer, (i.e., such as when the illumination source is the sun), the viewer distance along the observation axis, the area of the graphic film, along with the presence of any shading source define the size of the display and the number of colors visible from a given point. Given the great distance of the sun from the display surface the illumination angle doesn't appreciably vary from one side of a display to the other, thus, the change in observation angle is largely dependent on the viewer distance. The maximum width of a complete spectral display for the sun as a light source appears to be about one third the observation distance along the observation axis. Thus, for example, a viewer positioned in the center of the prismatic viewing ring about 3 meters from the center of a mounted graphic film of the invention which is

illuminated by the sun could see a spectral band as wide as about 1 meter wide, assuming the illuminated surface was unshaded and the graphic film area was at least one meter wide. If the sun is to the right of the observer's back when the observer is in the viewing ring, and the display area is large enough, (or the observer is close enough), such that more than one color is seen simultaneously, the longer wavelength colors will be on the right side of the illuminated area (toward the light source side) and the shorter wavelength colors will be on the left side of the illuminated area (away from the light source side). If the sun is to the left of the observer, then the longer wavelength colors will be on the left side of the display (again, toward the light source side) and the shorter wavelength colors will be on the right side of the display. This is due to the fact that when the light source is further away from the display than the observer, the observation angles on the side of the illuminated display toward the light source are always higher than the observation angles on the side of the illuminated display away from the light source. Under these same conditions, if the viewer walked along the observation angle axis toward the display, the visible spectrum area would become smaller, until the whole spectrum could be seen. As the viewer approaches still closer along the observation axis, the spectrum width eventually becomes smaller than the graphic film width, in which case the transmitted color of the reflective coating is visible on either side of the prismatic display.

If the source of illumination is closer than the viewer, i.e. such as when the display is illuminated by the headlights of a vehicle which is closer to the microsphere display than a viewer, then the relative position of the colors seen within the ring of the prismatic display is the reverse, owing to the fact that, under this condition the lower observation angles are always on the side of the display toward the light source. Also under this condition, the spectrum width of the display becomes smaller as the light source moves closer to the microsphere containing display surface, along the illumination axis.

When the light source distance along its axis is the same as the viewer distance along the observation axis, the viewer will see one color at any given point across the entire illuminated area containing the graphic film. From this point, any movement of the light source along the illumination axis or of the viewer, along the observation axis,

in either direction, will result in an increase in the number of colors seen in the illuminated area.

The thickness of the transparent microsphere bonding layer into which the transparent microspheres are embedded can vary. The coating must be thick enough such that the microspheres can be embedded to a depth of at least about 20% of the average diameter. There is no maximum thickness of the microsphere bonding layer as long as transparency is maintained.

The transparent microspheres should be embedded in the transparent bonding layer such that about 20% to about 80% of the average diameter is embedded, preferably about 30 to about 70%, most preferably about 40 to about 60%. If less than about 20% of the average diameter is embedded most of the prismatic display will be lost due to multiple internal reflections of the refracted light within each microsphere. Also, microspheres embedded at less than about 20% of the average diameter would be more likely to become detached from the bonding layer. If the microsphere layer is embedded too deeply, a prismatic display is not observed at higher illumination angles. Preferably, the only microspheres present are those partially embedded in the microsphere bonding layer. If some microspheres are completely embedded in the microsphere bonding layer, it will interfere with the prismatic display. The closer the refractive index of such completely embedded microspheres to the refractive index of the microsphere bonding layer, the less the interference.

The elements of the article of the invention can be varied to obtain the desired appearance. For example, transparent microspheres having different refractive indices can be bonded to the transparent bonding layer (i.e. on adjacent strips or areas, for example), to provide for a color contrast. Thus, when one section of the image is refracting the color blue to the viewer, for example, an adjacent section may be reflecting red, for example. This color contrast is a highly desirable feature and can be used to create the illusion of depth. Or the refractive index ratio of the microspheres to the bonding layer may be chosen so that the adjacent images are prismatically active at entirely different viewing angle ranges rather than overlapping viewing angle ranges to extend the viewing range of the display. In this way overlapping or multiple prismatic displays may be observed.

Another way to obtain the appearance described above (i.e. adjacent sections of contrasting color) is to coat microspheres of the same refractive index onto adjacent sections of bonding layers, which sections of bonding layer have different refractive indices. The same desirable type of color contrast and illusion of depth would be obtained.

Another means of altering the appearance of the article of the invention involves mixing together microsphere populations which are typically of the same or about the same diameter, but of different refractive indices, which are then bonded to the microsphere bonding layer, before printing some of the microspheres. The image observed by a viewer would be either two or more separate prismatic displays or two or more overlapping prismatic displays, depending upon the difference in refractive indices of the microsphere populations.

Another means of altering appearance would be to use multiple light sources at different illumination angles or light sources that move from one illumination angle to another, relative to a stationary viewer.

Microsphere Coating

The appearance of the graphic film of the invention can also be altered by forming a coating on some of the microspheres in between the microsphere surface and the reflective coating. The coating forms an image which is intended to contrast with the adjacent uncoated microspheres having only a reflective coating. The coating may be of similar composition and properties as the transparent microsphere bonding layer discussed previously. One or more coatings may be applied, some of which may overlap. The coatings may be applied side by side or one on top of another, for example. The coating or combination of coatings may vary in thickness or may have the same thickness when two coatings are present. One may be transparent and colorless and one may be transparent and colored. One may be opaque and the other transparent. Although the thickness of the coating can vary in areas, it is typically about 1/5 to about 1/50 of the average diameter of the microspheres.

If a transparent coating used to coat an image on some of the beads is also colorless, it has been observed that the type of visual contrast created is very

dependent on the thickness of the coating. (For the description of these visual effects a transparent coating with about a 1.5 refractive index was coated in the form of an image via a screen printing method on some of the 2.26 refractive index microspheres embedded in a 1.54 refractive index microsphere bonding layer, followed by vapor depositing about a 0.7 ohms/square surface resistance aluminum coating on the entire surface.)

If the transparent coating image is very thin, i.e., on the order of about one-tenth of the diameter of the microspheres or less, it interferes with the refraction angle and increases the viewing angle of the prismatic display i.e., it shifts the prismatic display away from the light source several degrees, thereby creating a color contrast with the adjacent areas of the image having only a reflective coating which exhibit a different color at the same viewing angle. If the viewer is positioned outside the viewing angle range of the prismatic display, this thin coating is darker in color than the unprinted area.

When the aforesaid coating was printed even thinner (less than about 1/20 the average diameter of the microspheres) through dilution with solvent and use of a higher mesh screen, it became barely visible, except within the viewing range of the prismatic display. Use of a thin transparent coating such as this provides the ability to create a hidden image or watermark effect, wherein the image is only visible within the viewing angle range of the prismatic display, where it surprisingly and suddenly appears to the viewer as their position changes relative to any illumination source.

As the coating thickness of said transparent coating image was increased beyond the order of one-tenth the diameter of the microspheres, while still preserving the spherical shape of the surface, the color of its prismatic display was seen to decrease and darken relative to the uncoated areas, i.e. the width of its prismatic display angular range was reduced and shifted to slightly higher viewing angles by several more degrees. At the same time the brightness of the image increased as the viewer moved outside the prismatic display range and nearer the illumination source. Additionally, the brighter image having the thicker coating was observed to be a photographic negative of the image observed within the annular ring of the prismatic display. Therefore, a viewer who starts near an illumination axis and then moves away

from the light source, increasing their viewing angle such that they progress into, and then through the range of the prismatic display, the aforesaid image can be seen to flip dramatically from a photographic negative to positive and then largely disappear at higher viewing angles. If the viewer moves in the opposite direction, the reverse is seen. The same effect is also achieved by moving the illumination source while the viewer and substrate remain stationary, or by moving the substrate and holding the viewer and illumination source stationary.

As the thickness of the transparent coating on some of the microspheres is increased, the observed loss of color within the viewing angles of the prismatic display, and the appearance of increasing brightness nearer the illumination source, is believed to be due to the approach of the catadioptric lens system created by the microsphere and the transparent coating (which somewhat conforms to the spherical shape of the microsphere) to what is referred to in the art of optics as the lens focal point. As the lens focal point is approached, a reversal of the color dispersion caused by the higher index glass microsphere appears to takes place with a conversion of at least a portion of that dispersed light to a retroreflected image.

The maximum color shift which should be obtainable via the process of coating a thin transparent coating in between the microspheres and the reflective coating for a given combination of microsphere and microsphere bonding layer refractive index is difficult to define. It is theorized that the shift cannot be any larger than the width of the annular prismatic display defined by the microsphere and microsphere bonding layer refractive index ratio, i.e., 15-20 degrees. Although actual observed shift in the limited range of materials observed to date has been limited to about 5 degrees. It is believed that as the transparent coating thickness on some of the microspheres increases, the valleys in between the microspheres begin filling up and therefore, as one proceeds from the illumination source toward higher viewing angles, the portion of the microsphere surface involved in the reflection of the refracted light, which is naturally further away from the apex because of increasing refraction angle, becomes covered by the coating filling the valleys. It is therefore possible that higher viewing angle shifts would take place if the coating was only present on the upper portion of the microspheres, or if the bead embedment was low such that a larger reservoir exists in

the valleys between the microspheres. It is believed that all such methods of adjusting the coating to optimize the resulting desired decorative effects can be used.

Definition of the exact limits of the above described effects for purposes of the specification is further complicated by the variables inherent in the process of coating on a spherically shaped surface, where the coating thickness can vary from the apex of the microspheres to the valleys in between, as well as variables caused by printing method, shrinkage characteristics and evaporative rates of the chosen coating. One skilled in the art of printing should be able to quickly define the ideal coating and process variables empirically, given the above description of potential effects and reference to the examples herein provided. A suggested starting point would be to choose a transparent coating of the same type as the transparent microsphere bonding layer itself. For a subtle watermark effect, one starts at the minimum dilution level allowed by the chosen printing process, and adjusts the printing parameters to minimize coating thickness on the microspheres and observes the visual effects relative to the desired effect after coating the reflective coating. If the result is more subtle than desired, the process and dilution strength would be adjusted to result in a thicker coating or vice versa. If a lens focal point is desired, one increases the coating thickness until the desired amount of highlight is seen near the illumination source.

An additional visual effect can be created when a thin transparent coating is colored with a finely dispersed pigment or dye which will retain sufficient transparency to not mask the prismatic display. In this case, the chosen color will act as a filter for the color of the prismatic display. For example, if the colored transparent coating is red, the prismatic display will enhance the red color at the viewing angle where red is refracted. At the viewing angle where blue is refracted, the red and blue will mix to result in a purple color and so on. The actual color will vary depending on the level of transparent red pigment, its hue and color strength and the intensity of the illumination source. For example, a strong red color will be less affected by the prismatic display at low illumination. If one chooses to use a larger diameter microsphere and a lower viscosity coating, the valleys in between the microspheres can allow a fairly thick color coat reservoir, while still maintaining the spherical shape of the surface and hence the

prismatic display. This is particularly effective for darker pigments such as carbon black.

Still further complex visual effects can be obtained by varying the thickness of the coating on some of the microspheres relative to the others while leaving still others uncoated, or by using colored coating(s) in combination with colorless coating(s). The aforesaid coating variation can be achieved by overprinting a portion of the image with one or more additional layers or by printing a graduated halftone, diffusion dither halftone or stochastic halftone which distributes a greater or lesser amount of coating depending on the type of printing method. For example, when a graduated halftone is screen printed the screen masking is photographically developed to result in more or less open screen area in different image areas. By proper choice of coating refractive index, dilution strength and screen mesh, one can vary the thickness of the coating between the range of visual effects described above in less printing steps, such that portions of the image have subtle contrast and portions are at the lens focal point. Since the color contrast changes as a function of viewing angle, one can also provide pseudo 3-dimensional effects by the printing of drop shadows with varying coating thickness or by generating graduated grayscale halftone screens from photographs of 3-dimensional objects. For example, if a positive image of a grayscale converted photograph is printed with a colored transparent ink and then overprinted with the negative grayscale converted image using a colorless ink, wherein the second image is printed slightly off-register, a 3-dimensional effect can be created, after coating the metallic reflector layer. Still other effects are possible given the disclosure of the above-described principles of controlling the dispersed color.

Examples of suitable coatings include but are not limited to those selected from the same group as the aforesaid transparent microsphere bonding layer. If the coating is to be colored via addition of dispersed pigments or dyes, as is well known in the graphics arts industry, a preferred group of coatings would include vinyl polymers or vinyl copolymers; acrylic polymers or copolymers; vinyl/acrylic blends, polyurethanes, including water-based dispersions; polyesters; epoxies, ethylene acrylic acid and water dispersions and blends thereof; and other materials which are capable of dispersing pigments or are typically compatible with dyes. Adhesion promoters such as silanes,

titanates, organo-chromium complexes or the like may be added to improve adhesion to the glass microsphere surface.

Reflective Coating

The reflective coating is a mirror-like layer which is formed on both the surfaces of the microspheres embedded in the microsphere bonding layer and on the microsphere coatings formed on some of the microspheres. It is typically a metallic coating formed by high vacuum vapor deposition of heated metals like aluminum, tin, gold, chromium, stainless steel, indium or the like. It can also be formed by chemical reduction of an ionic solution of a metal such as silver. It can also be a transparent dielectric mirror as generally described in Bingham, U.S. Pat. No. 3,700,305. Such coating can be formed by first vapor-coating a layer of cryolite (Na_2AlF_6) in an optical thickness (the product of physical thickness and index of refraction) corresponding to about one-quarter wavelength of white light (i.e., about one-quarter of 5500 angstroms), followed by vapor-coating a one-quarter-wavelength-thick layer of zinc sulfide over the layer of cryolite. Vapor deposited aluminum is a preferred coating because of its low cost and bright color. The reflecting layer is preferably opaque, to maximize its reflecting qualities and minimize the transmitted color effects of the adhesive and/or substrate layers beneath it. Since the vapor deposited metal coating is very thin, typically on the order of 300 angstroms or greater, more typically 300 to 1000 angstroms, and thickness is difficult to measure on such a convoluted surface, those skilled in the art of metallic vapor deposition typically use a surface measurement of electrical resistivity, such as that described in American Society of Testing Materials (ASTM) D257. For aluminum, a coating thickness of about 0.7 ohms/square surface provides an adequate opaque mirror-like reflecting surface.

Pressure-Sensitive Adhesive

A layer of adhesive such as, for example, a pressure sensitive adhesive, may be affixed on the side of the reflective coating opposite the microsphere layer. The adhesive may be permanent, repositionable, etc. depending upon the application. The term adhesive as used herein also includes adhesive films which may be permanent,

repositionable, and etc. An easily removable and repositionable adhesive would be useful for providing temporary graphic films.

Examples of suitable adhesives include but are not limited to those selected from the group consisting of acrylic polymers and copolymers, such as isooctyl acrylate/acrylic acid copolymers, modified acrylic copolymers, polyesters such as polyvinyl acetate, and its copolymers, polyurethanes, epoxies, highly plasticized vinyls or vinyl copolymers, copolymers of ethylene with acrylic acid and methacrylic acid and its metal salt modified polymers. This layer does not play a role in the prismatic display and merely serves to bind the article to a substrate upon removal of the optional release liner. Also anticipated by the invention is the use of a primer layer in between the reflective coating and the adhesive or a barrier layer which protects the reflective coating from interacting with acidic or basic components in the adhesive.

Optional Transparent Film

A transparent film may optionally be affixed to the transparent microsphere bonding layer opposite the side in which the microsphere layer is embedded. The film should preferably demonstrate flexibility, tear resistance, and weatherability in addition to its transparency.

Examples of suitable transparent films include but are not limited to those selected from the group consisting of elastomers, polyolefins, polyurethanes, polyesters, impact modified acrylics, plasticized vinyls, etc. As with the optional transparent adhesive layer, this optional layer does not effect the viewing angle of the prismatic display.

Release Liner

The optional release liner useful in the article the invention can be formed from a variety of materials including, but not limited to, those selected from the group consisting of silicone coated paper or film, fluorocarbon coated paper or film, polyethylene or polypropylene coated paper or film and polyester terephthalate film. The primary requirement of this layer is to demonstrate low peel adhesion to the adhesive to allow separation.

The present invention will be better understood by referring to Figs. 1 to 9.

Fig. 1 illustrates a cross-section of a known rainbow sheeting which provides a transparent film layer 2 attached to a first surface of a microsphere binding layer 4, a layer of transparent microspheres 6 at least partially embedded in a second surface of the microsphere bonding layer 4, and a reflective coating 8 covering the surfaces of the microspheres 6 not embedded in the microsphere bonding layer 4, an adhesive layer 10 adhered to the reflective coating 8, and a release liner 12 attached to the adhesive layer 10.

Light ray 14 passes through transparent film layer 2 and transparent microsphere binding layer 4. At the interface of the bonding layer 4 and microsphere 6 the light ray 14 is refracted into colored light rays 16 and 18 which pass through the microsphere 6 where they reach the perimeter of the microsphere 6 and are reflected by reflective coating 8 back through microsphere 6, bonding layer 4, and film layer 2, where they can be observed by a viewer.

One embodiment of the invention illustrated by Fig. 2 provides a transparent film layer 20 attached to a first surface of a microsphere bonding layer 22, a layer of transparent microspheres 24 at least partially embedded in a second surface of the microsphere bonding layer 22, a transparent coating 28 on some of the microspheres the transparent coating 28 being on surfaces of the microspheres 24 not embedded in the microsphere bonding layer 22, a reflective coating 30 coated over the transparent coating layer 28, and elsewhere coated directly over the surfaces of the microspheres 24 not embedded in the microsphere bonding layer 22, an adhesive layer 32 adhered to the reflective coating 30, and a release liner 34 attached to the adhesive layer 32.

Light ray 36 passes through transparent film layer 20 and transparent microsphere bonding layer 22. At the interface of the bonding layer 22 and microsphere 24 the light ray 36 is refracted into colored light rays 38 and 40 which pass through the microsphere 24 where they reach the perimeter of the microsphere 24 and are reflected by the reflective coating 30 back through microsphere 24 bonding layer 22, and film layer 20 where they are observed by a viewer.

Light ray 42 passes through transparent film layer 20 and transparent microsphere bonding layer 22. At the interface of the bonding layer 22 and

microspheres 24 the light ray 42 is refracted into colored light rays 44 and 46 which pass through the microsphere 24 and the transparent coating 28 where they reach the perimeter of the transparent coating 28 and are reflected by the reflective coating 50 back through the transparent coating 28, the microsphere 24, the bonding layer 22, and film layer 20 where they are observed by a viewer.

In preparing the graphic film of Fig. 2, a thin transparent coating 28 is printed on the back surface of a selected portion of the non-embedded glass microspheres before the reflective coating is applied, to create an image thereon. The reflective coating 30 is then applied over the whole surface. The printed transparent coating has been found to shift the dispersion angle of the reflected rainbow by up to several degrees away from the light source, such that visible light ray 36, which enters the sheeting at the same angle as visible light ray 42, is dispersed such that the blue and red spectral components 44 and 46 exit the sheeting at angles slightly greater than the corresponding rays 38 and 40. This creates a contrasting image to the background image of the rainbow reflected in the unprinted portion of the transparent microspheres. If the printed transparent coating is very thin, i.e. less than about 1/10th of the diameter of the glass microsphere, the observation angle is only slightly shifted, resulting in a subtle image, much like a watermark, which is visible only in the range that the rainbow dispersion takes place as both the printed and unprinted background images progress through the color spectrum from violet to red and maintain a visible contrast as both change color. As the transparent coating printed on the glass microspheres is increased in thickness to about 1/5th the diameter of the glass microspheres, the image darkens at the viewing angles where the unprinted portion is exhibiting the rainbow. At the same time the visibility of the printed area increases as the viewer moves closer to the light source as a highlight image mirroring the color of the light source, meaning a portion of the dispersed light is converted to retroreflected light and the printed area approaches the focal point of the lens created by the bead. This is illustrated by Fig. 3, wherein the color dispersion of visible light ray 68, entering the sheeting at the same angle as ray 42 in Fig. 2 is reflected back to the viewer as light ray 70. The visual effect of the thicker coating is that the printed image appears as a photopositive near the light source and switches to a photonegative in the

dispersed color viewing angle range. If the coating thickness is increased beyond the focal point of the retroreflected lens the image takes on the color of the reflective coating at all viewing angles.

One embodiment of the graphic film of the invention illustrated by Fig. 3 provides a transparent film layer 48 attached to a first surface of a microsphere bonding layer 50, a layer of transparent microspheres 52 at least partially embedded in a second surface of the microsphere bonding layer 50, a transparent coating 54 in the form of an image on the portion of the microspheres not embedded in the microsphere bonding layer 50, and a reflective coating 56 coated over the transparent coating layer 54 where present and elsewhere coated directly over the microsphere 52 surface not embedded in the microsphere bonding layer 50, an adhesive layer 58 adhered to the reflective coating 56, and a release liner 60 attached to the adhesive layer 58.

Light ray 62 passes through transparent film layer 48 and transparent microsphere bonding layer 50. At the interface of the bonding layer 50 and microspheres 52 the light ray 62 is refracted into colored light rays 64 and 66 which pass through the microsphere 52 where they reach the perimeter of the microsphere 52 and are reflected by the reflective coating 56 back through microsphere 52, bonding layer 50, and film layer 48 where they are observed by a viewer.

Light ray 68 passes through transparent film layer 48 and transparent microsphere bonding layer 50. At the interface of the bonding layer 50 and microspheres 52 the light ray 68 is refracted into colored light rays which pass through the microsphere 52 and the transparent coating 54 where they reach the perimeter of the transparent coating 54 and are reflected by the reflective coating 56 back through the transparent coating 54, the microsphere 52 where the dispersion is reversed and the light passes through bonding layer 50, and film layer 48 where it is observed by a viewer as 70, a retroreflected ray.

One embodiment of the graphic film of the invention illustrated by Fig. 4 provides a transparent film layer 74 attached to a first surface of a microsphere bonding layer 76, a layer of transparent microspheres 78 and 80 at least partially embedded in a second surface of the microsphere bonding layer 76, a reflective coating 82 on the surfaces of the microspheres 78 and 80 not embedded in the microsphere

bonding layer 76, an adhesive layer 84 adhered to the reflective coating 82 and a release liner 86 attached to the adhesive layer 84. Transparent microspheres 78 and 80 have differing refractive indices resulting in a color contrast observed by a viewer as light is shined on the article.

Light ray 88 passes through transparent film layer 74 and transparent microsphere bonding layer 76. At the interface of the bonding layer 76 and microspheres 78 the light ray 88 is refracted into colored light rays 90 and 92 which pass through the microsphere 78 where they reach the perimeter of the microsphere 78 and are reflected by the reflective coating 82 back through the microsphere 78, the bonding layer 76, and film layer 74 where they are observed by a viewer.

Light ray 94 passes through transparent film layer 74 and transparent microsphere bonding layer 76. At the interface of the bonding layer 76 and microspheres 80 the light ray 94 is refracted into colored light rays 96 and 98 which pass through the microsphere 80 where they reach the perimeter of the microsphere 80 and are reflected by the reflective coating 82 back through the microsphere 80, the bonding layer 76, and film layer 74 where they are observed by a viewer.

One embodiment of the graphic film of the invention illustrated by Fig. 5 provides a transparent film layer 100 attached to a first surface of a microsphere bonding layer 102 and 106, a layer of transparent microspheres 104 at least partially embedded in a second surface of the microsphere bonding layers 102 and 106, a reflective coating 108 on the surfaces of the microspheres not embedded in the microsphere bonding layers 104 and 106, an adhesive layer 110 adhered to the reflective coating 108, and a release liner 112 attached to the adhesive layer 112. Microsphere bonding layer sections 102 and 106 have differing refractive indices resulting in a color contrast observed by a viewer as light is shined on the graphic film.

Light ray 114 passes through transparent film layer 100 and transparent microsphere bonding layer 102. At the interface of the bonding layer 102 and microspheres 104 the light ray 114 is refracted into colored light rays 116 and 118 which pass through the microsphere 104 where they reach the perimeter of the microsphere 104 and are reflected by the reflective coating 108 back through

microsphere 104, bonding layer 102, and film layer 100 where they are observed by a viewer.

Light ray 120 passes through transparent film layer 100 and transparent bonding layer 106. At the interface of the bonding layer 106 and microsphere 104 the light ray 120 is refracted into colored light rays 122 and 124 which pass through microsphere 104 where they reach the perimeter of the microsphere 104 and are reflected by the reflective coating 108 back through microsphere 104, bonding layer 106, and film layer 100 where they are observed by a viewer at an angle different from light rays 116 and 118.

One embodiment of the graphic film of the invention illustrated by Fig. 6 provides a transparent film layer 126 attached to a first surface of a microsphere bonding layer 128, a layer of transparent microspheres 130 and 132 at least partially embedded in a second surface of the microsphere bonding layer 128, a transparent coating 134 on some of the surfaces of the microspheres not embedded in the microsphere bonding layer 128, a reflective coating 136 coated over the transparent coating layer 134 where present and elsewhere directly over the surfaces of the microspheres 130 and 132 not embedded in the bonding layer 128, an adhesive layer 138 adhered to the reflective coating 136, and a release liner 140 attached to the adhesive layer 138. Microspheres 130 and 132 have different refractive indices and thus reflect light rays differently.

Light ray 142 passes through transparent film layer 126 and transparent microsphere bonding layer 128. At the interface of the bonding layer 128 and microspheres 130 the light ray 142 is refracted into colored light rays 144 and 146 which pass through the microspheres 130 where they reach the perimeter of the microsphere 130 and are reflected by the reflective coating 136 back through the microsphere 130 the bonding layer 128, and film layer 126 where they are observed by a viewer.

Light ray 160 passes through transparent film layer 126 and transparent microsphere bonding layer 128. At the interface of the bonding layer 128 and microspheres 132 the light ray 160 is refracted into colored light rays 162 and 164 which pass through the microsphere 132 where they reach the perimeter of the

microsphere 132 and are reflected by the reflective coating 136 back through the microsphere 132, the bonding layer 128, and film layer 126 where they are observed by a viewer.

Light ray 148 passes through transparent film layer 126 and transparent microsphere bonding layer 128. At the interface of the bonding layer 128 and microsphere 130 the light ray 148 is refracted into colored light rays 150 and 152 which pass through the microsphere 130 and the transparent coating 136 where they reach the perimeter of the transparent coating 134 and are reflected by the reflective coating 136 back through the transparent coating 134, the microsphere 130, the bonding layer 128, and film layer 126 where they are observed by a viewer.

Light ray 159 passes through transparent film layer 126 and transparent microsphere bonding layer 128. At the interface of the bonding layer 128 and microsphere 132 the light ray 160 is refracted into colored light rays 156 and 158 which pass through the microsphere 132 and the transparent coating 134 where they reach the perimeter of the transparent coating 134 and are reflected by the reflective coating 136 back through the transparent coating 134, the microsphere 132, the bonding layer 128, and film layer 126 where they are observed by a viewer.

Thus, four contrasting colors can be observed by a viewer of Fig. 6, upon proper selection of the components.

Fig. 8 is a plan view of a graphic film 170 of the invention having a 3-dimensional appearance formed by successive printing of two images 172 and 174 with a transparent coating on the transparent microspheres under the reflective coating. The images 172 and 174 are printed slightly out of registry such that areas of double printing 176 result in combination with unprinted areas 178 bounded between single printed images 172 and 174. The images change from photo-positive to photo-negative 3-dimensional appearances depending on a viewer's position relative to a source of light.

Fig. 9 is a cross-section of the printed images of Fig. 8 taken along line 9-9 of Fig. 8, such images formed on the sheeting of Fig. 2. The graphic film of Fig. 9 comprises a transparent film layer 34 attached to a first surface of a microsphere bonding layer 32, a layer of transparent microspheres 24 at least partially embedded in

a second surface of the microsphere bonding layer 32, a transparent coating 28 and 28a in the form of an image on the portion of the microspheres not embedded in the microsphere bonding layer 32, and a reflective coating 30 coated over the transparent coating layers 28 and 28a where present and elsewhere coated directly over the microsphere 24 surface not embedded in the microsphere bonding layer 32, an adhesive layer 22 adhered to the reflective coating 30, and a release liner 20 attached to the adhesive layer 20. Transparent coatings 28 and 28a are printed such that areas of double thickness 28a exist in combination with unprinted areas and single printed areas 28.

Examples

The following Examples further illustrate but do not limit the present invention. All parts, percentages, ratios, etc. in the Examples and the rest of the specification are by weight unless indicated otherwise.

Example 1

A 40 micrometer thick film of Surlyn™ 1705 Ionomer, a thermoplastic copolymer of ethylene and methacrylic acid containing a zinc ionic crosslinking agent, available from Dupont, and having a measured refractive index of about 1.505 was cast via thermoplastic extrusion onto a 90 micron thick, biaxially oriented and heat stabilized film of polyethylene terephthalate (PET). A length of this web was placed in a 120°C oven and coated with a rolling cascade of 2.26 refractive index glass microspheres having a mean diameter of about 70 micrometers, with a ± 10 micrometer distribution. The microspheres had also been surface treated with an organo-chromium complex to aid adhesion. At this temperature the film surface was tacky and adhered to the microspheres so that a uniform monolayer of the microspheres was present on the film surface. The web was then placed in a 190°C oven for 1.5 minutes, such that the film melted and the microspheres were embedded to about 45-55% of their mean diameter by surface wetting forces. The microsphere coated film was cooled to room temperature and screen printed with an image using a

230 mesh polyester filament screen, using a 23% solids transparent coating solution made from the following ingredients:

Resin Solids

26.65% Union Carbide VYNS3, a vinyl chloride/vinyl acetate copolymer resin

9.87% Union Carbide VAGH, a partially hydrolyzed vinyl chloride/vinyl acetate copolymer resin

5.3.30% Rohm & Haas Acryloid™ B44, an acrylic copolymer resin

3.60% C.P. Hall Paraplex™ G-62, an epoxidized soybean oil plasticizer

4.30% BASF Uvinol™ N-539, a substituted acrylonitrile ultraviolet light absorber

1.78% Witco Nuostab™ v-1923, a calcium-zinc salt heat stabilizer

0.25% Union Carbide A-1130, a triaminofunctional silane adhesion promoter

0.07% General Electric SF96, a polymethyl siloxane flow control agent

Solvent Blend

40.2% Cyclohexanone, 26.8% Diethylene glycol monoethyl ether acetate, 17.5% N-methyl pyrrolidone, 15% mixed aromatic hydrocarbons, 65°C flashpoint.

The printed image was dried at about 75°C for 10 minutes in a convection oven. A separately cast and dried film from the solution had a refractive index as measured by an Abbe refractometer of about 1.518. The printed film was then placed in a Denton DV-515 high vacuum metalizer at about 1X10-6 torr and coated with an opaque layer of aluminum which measured 0.7 ohms/sq. resistance according to ASTM D257. A 25 micron thick pressure sensitive adhesive cast on a silicone release paper was then laminated to the metalized surface of the sheet. The adhesive was a free radical solution polymerized terpolymer comprising by weight 70% isooctyl acrylate, 22.5% methyl acrylate and 7.5 % acrylic acid, having an intrinsic viscosity of about 0.6, and cast out of a 42% solids ethyl acetate solution to which had been added by weight, 1.5% azo-bis-isobutyronitrile. Finally, the PET carrier was stripped.

By reference to Fig. 7, previously described, the resulting graphic sheet 262 was laminated to a flat paint panel substrate 260 and placed in an area having low illumination and further illuminated with a focused flashlight 266 placed perpendicular

to the surface at a distance of about 2 meters. The light source 266 was placed on line segment 274, the substrate axis, perpendicular to the surface, meaning the entrance or illumination angle 276 was zero degrees. A viewer 264, positioned on axis 268 slightly closer to the substrate than the light source and at 10 degrees observation angle 272 saw the printed area was a slightly darker gray-silver color than the unprinted area, thereby rendering a subtle image. As the viewer moved away from the illumination axis (angle 272 increasing) he observed the violet color of the rainbow in the unprinted area starting at about 24 degrees observation angle, while observing the violet color of the rainbow in the printed area at about 27 degrees observation angle. At 27 degrees the color of the unprinted area had progressed to the blue color of the rainbow, thereby creating a contrast with the violet color of the printed area. As the viewer moved still further away from the light source to about 41 degrees observation angle, he saw the unprinted area progress through the colors of the rainbow going from violet to blue to green to yellow and then red. At about 40 degrees, the printed areas of the graphic film were a yellow color, which were in contrast to the red color of the unprinted areas. At about 42 degrees observation angle, the unprinted background returned to a gray-silver color while the printed portion was red. Above about 43 degrees observation angle the printed background returned to a gray-silver color which was slightly darker than the unprinted area, similar to the contrast seen at 10 degrees observation angle.

Example 2

A printed graphic film was prepared according to the method of Example 1 with the exception that a 110 mesh polyester fabric screen was used to print the image prior to vapor coating with aluminum, lamination to the pressure sensitive adhesive, stripping of the PET and mounting to a substrate panel. In this case, a viewer standing at 10 degrees observation angle relative to the light source saw a bright highlight image corresponding to the printed area which was in contrast to the light gray-silver of the unprinted background. At about 24 degrees observation angle the violet color of the unprinted background was visible, but the printed image area started to darken. As the observation angle increased, the image of the printed area continued to darken as the

unprinted area progressed through the rainbow colors. The net affect of this contrast change was that the image near the light source went from a photonegative character to a photopositive character. At about 42 degrees observation angle the unprinted area returned to its original gray-silver appearance. The printed image also turned this color, meaning above 43 degrees observation angle the printed image disappeared into the background, yielding a surprising decorative effect.

Example 3

Two printing screens were prepared out of 157 mesh polyester screening material, using conventional photoemulsion techniques. The first screen was the photopositive of the block letter "H", meaning the background of the image contained stenciling and the block letter "H" was unstenciled. The letter had a 152.5 mm height and a 25 mm stroke width. The second screen was an 6.5 mm outline of the letter "H", such that the interior dimension of the outline letter was the outside dimension of the first letter. In other words, a 25% negative enlargement of the first letter was superimposed over the photopositive of the original screen. These screens were used to print the microsphere coated film of Example 1, by printing the solution of Example 1 in sequence, with drying in between, such that the second print was registered 3 mm off of the first at a 45 degree angle. The net result was the creation of what is referred to in the graphic arts industry as a "drop shadow", as depicted in Figure 8. In this instance portions of the first printed image were overlapped to result in a double thickness which happened to be at the focal point of the lens. The printed film was then vapor coated with aluminum, laminated to adhesive, stripped of the PET and mounted to a substrate panel as in Example 1. A viewer moving from 0 - 45 degrees observation angle relative to a light source saw a 3-dimensional appearing "H" which demonstrated a photo-reversal of the image. The constantly changing color contrast of the rainbow provided a decorative effect.

Example 4

A sheet of the 40 micron thick Surlyn™ 1705 Ionomer film extrusion cast on 90 micron heat stabilized PET film used in Example 1 was screen printed on the

Surlyn™ side with an image using a 110 mesh polyester screening material and the following solution at 35% solids.

Resin Solids:

88.87% Dutch State Mines Uralac™ CP1049 SU, a urethane extended polyester resin

9.10% Monsanto Resimene™ 881, a partially butylated melamine formaldehyde resin

2.00% Tinuvin 328, a Benzotriazole type ultraviolet (UV) light absorber from Ciba-Geigy

0.03% General Electric SF-96, a polymethyl siloxane flow control agent

Solvent Blend

77.9% Mixed aromatic hydrocarbons, 65°C flashpoint, 14.2% Diethylene glycol monoethyl ether acetate, 5.3% Xylene, 2.6% Butanol

A separately coated, dried and cured film from this solution had a refractive index of about 1.533. The printed image was dried at 74°C for 10 minutes. Subsequently, the entire sheet was placed in a 100°C oven and cascade coated with a monolayer of the 2.26 refractive index microspheres of Example 1. The sheet was then placed in a 150°C oven for 1 minute and a 190°C oven for 1.5 minutes to partially encapsulate the microspheres in both the melamine polyester and Surlyn™ areas and to cure the melamine polyester.

The microsphere coated sheet was then vapor coated with aluminum, laminated to adhesive, stripped of PET and mounted as in Example 1. When viewed as described in Example 1, the printed area, having a 1.533 refractive index, reflected a rainbow from about 27 to 43 degrees observation angle relative to the unprinted area having a refractive index of about 1.505 which reflected a rainbow from about 24-42 degrees. Thus the image was in color contrast to the background as the rainbow colors progressed due to changing viewing angle. At about 10 degrees the printed area was slightly darker in appearance. Above 45 degrees, the relative contrast was reduced, meaning the image almost disappeared.

Example 5

An image in the form of the letter "H" was cut from a graphic pressure sensitive prespacing tape (available from 3M Company as SCPM-2 Prespacing Tape) and laminated to a sheet of the 40 micron thick Surlyn™ 1705 Ionomer film extrusion cast on 90 micron heat stabilized PET film used Example 1, on the Surlyn™ side. The resulting sheet was placed in an oven at 120°C and cascade coated with the 2.26 average refractive index microspheres of Example 1. The film was then cooled to room temperature and the premask carefully removed to expose uncoated Surlyn™ film surface. The sheet was then placed in a 120°C oven and cascade coated with 2.19 average refractive index glass microspheres treated similarly to the 2.26 microspheres. The sheet was then placed in a 190°C oven for an additional 1.5 minutes to partially encapsulate the microspheres. The microsphere coated sheet was then vapor coated with aluminum, laminated to adhesive, stripped of the PET and mounted as in Example 1. When viewed as described in Example 1, the image containing the 2.19 index microspheres reflected a rainbow from about 30 degrees to about 47 degrees, which was in color contrast to the rainbow reflected from the 2.26 refractive index microspheres at about 24 to 42 degrees. At observation angles less than about 23 degrees and greater than about 48 degrees the image was largely invisible.

While this invention has been described in connection with specific embodiments, it should be understood that it is capable of further modification. The claims herein are intended to cover those variations which one skilled in the art would recognize as the equivalent of what has been described herein.

CLAIMS:

1. A graphic film comprising:

(a) a layer of transparent solid glass microspheres bonded to a transparent microsphere bonding layer, wherein the microspheres are partially embedded in the transparent microsphere bonding layer, wherein about 20% to about 80% of the average diameter of each microsphere is embedded in the transparent microsphere bonding layer, and wherein the ratio of the transparent microsphere refractive index to the transparent microsphere bonding layer refractive index is about 1.3:1 to about 1.7:1;

(b) at least one non-reflective coating in the form of an image on some of the microspheres wherein said coating(s) is on surface(s) of the microspheres not embedded in the transparent microsphere bonding layer;

(c) a reflective coating coated on the surfaces of the microspheres not embedded in the transparent microsphere bonding layer, wherein for the microspheres coated with the non-reflective coating(s) of element (b), the reflective coating is coated over the non-reflective coating(s) of element (b);

(d) an optional adhesive layer affixed on the side of the reflective coating opposite the microsphere layer;

(e) an optional transparent release liner affixed to the adhesive layer, when present; and

(f) an optional transparent film affixed to the bonding layer opposite the side in which the microsphere layer is embedded.

2. The graphic film of claim 1 wherein the microspheres have an average diameter of about 60 to about 90 microns.

3. The graphic film of claim 1 which exhibits either visibly overlapping or discrete multiple prismatic displays from a single illumination source.

4. The graphic film of claim 1 which exhibits a 3-dimensional appearing prismatic display.

5. The graphic film of claim 1 wherein about 30 to about 70% of the average diameter of each microsphere is embedded in the transparent bonding layer.

6. The graphic film of claim 1 which exhibits an image change from a photopositive to a photonegative, or from a photonegative to a photopositive, as a viewer changes position relative to a single illumination source.

7. The graphic film of claim 1 wherein the non-reflective coating(s) of element (b) is colorless and transparent.

8. The graphic film of claim 1 wherein the ratio of the transparent microsphere refractive index to the transparent microsphere bonding layer refractive index is about 1.35 to about 1.55.

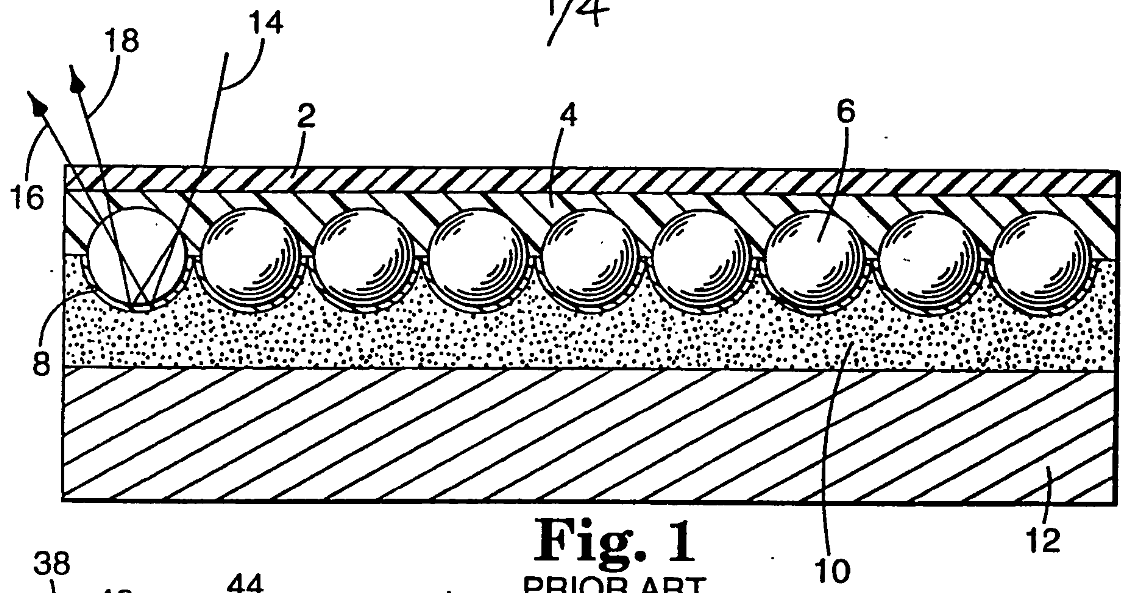

Fig. 1
PRIOR ART

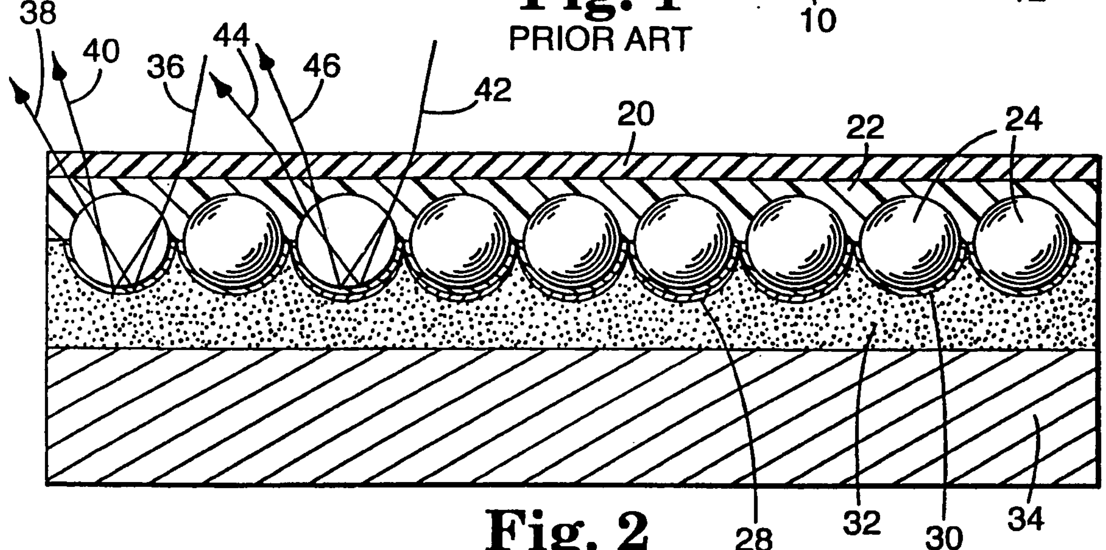

Fig. 2

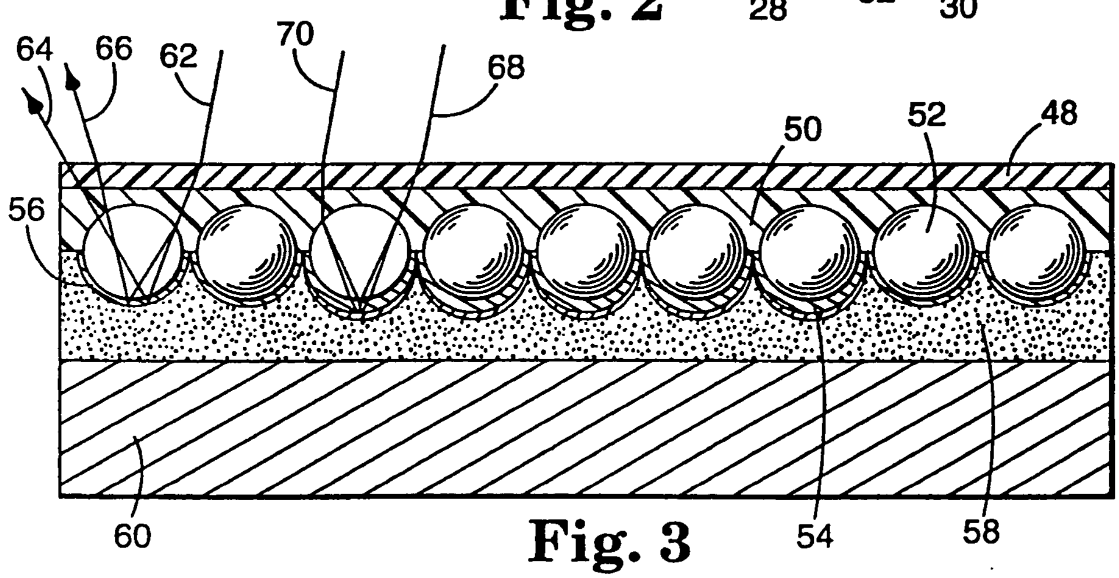

Fig. 3

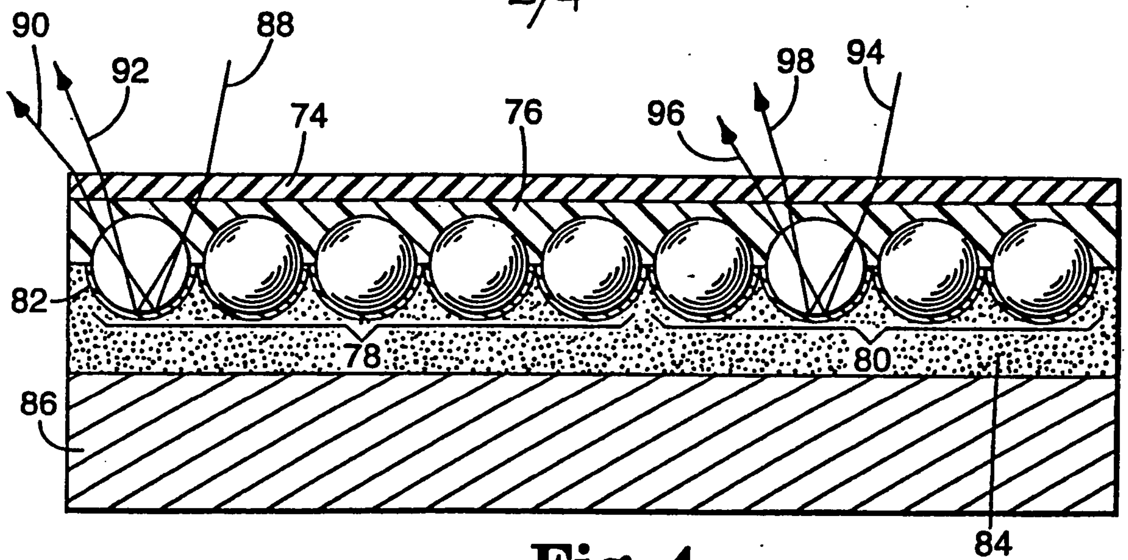

Fig. 4

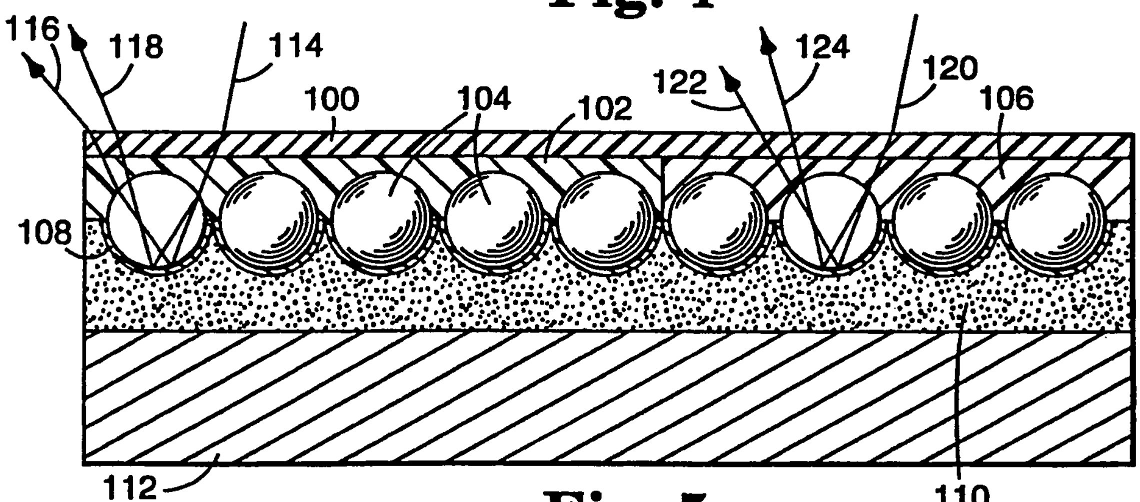

Fig. 5

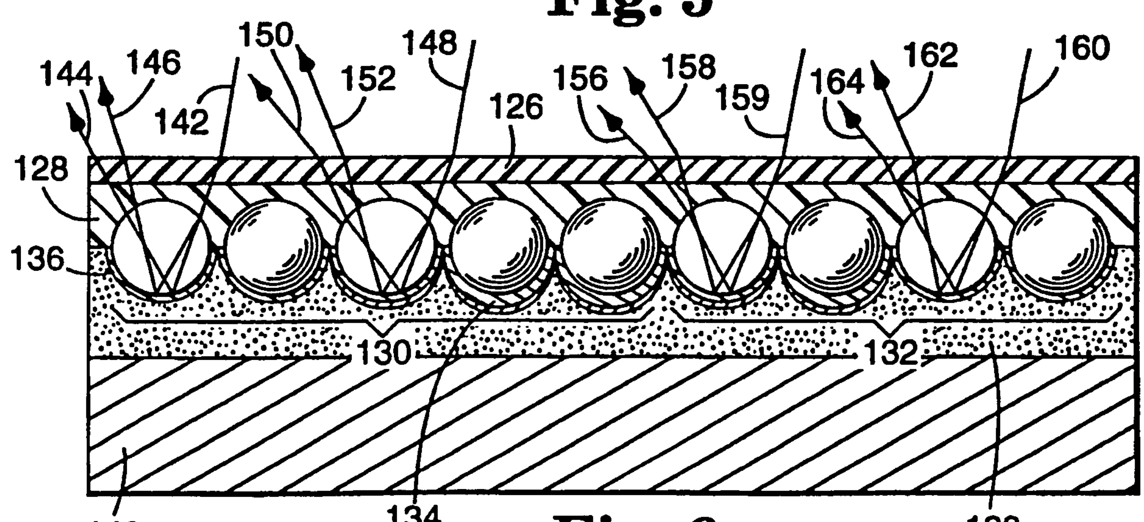

Fig. 6

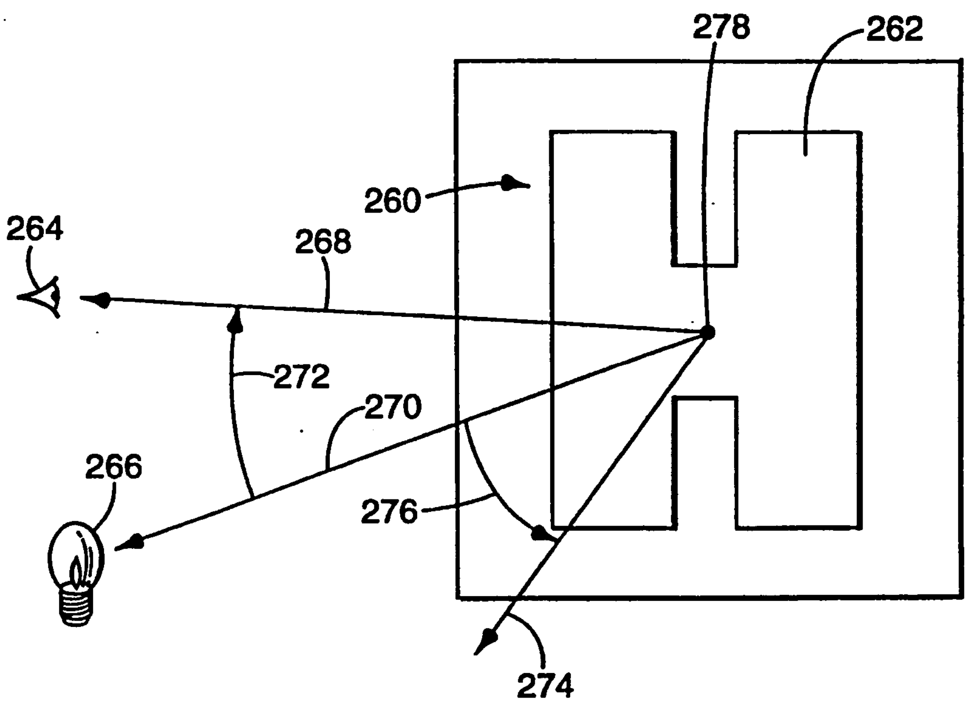

Fig. 7

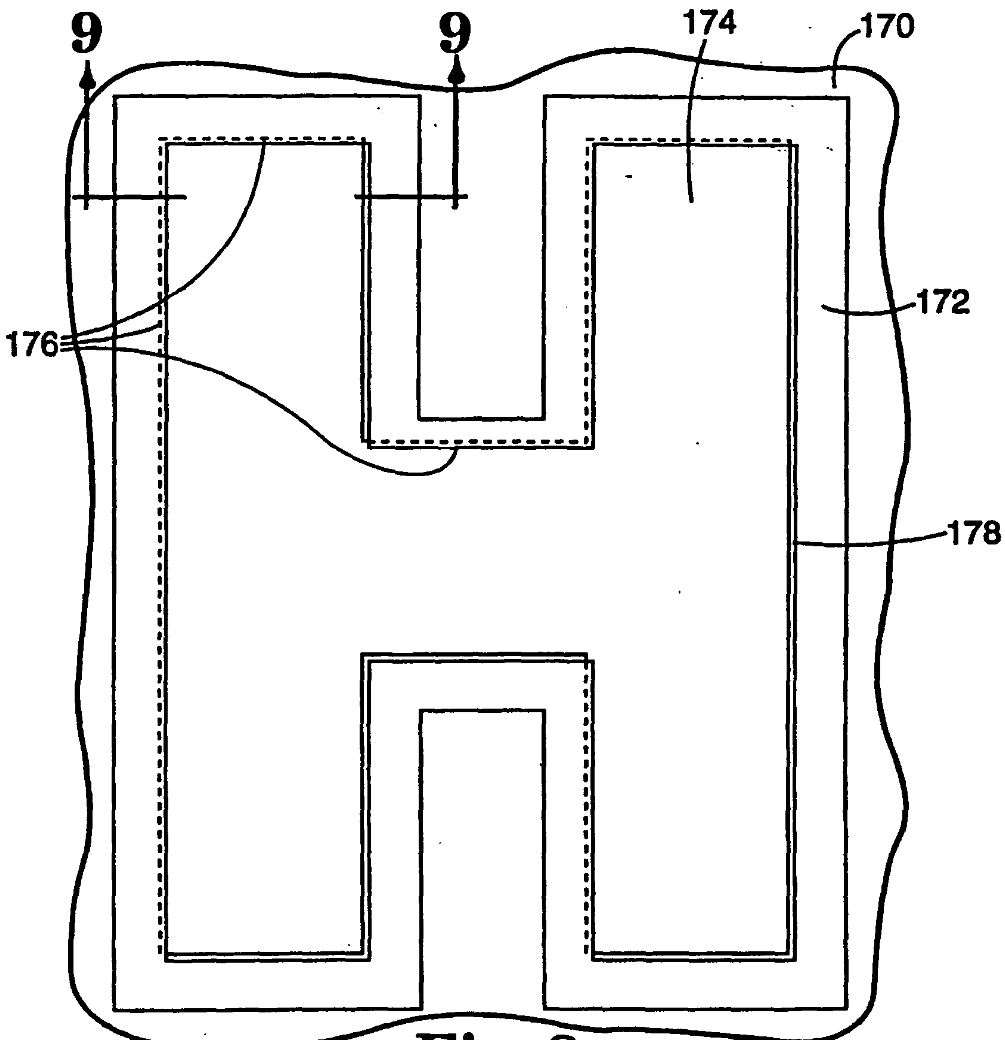

Fig. 8

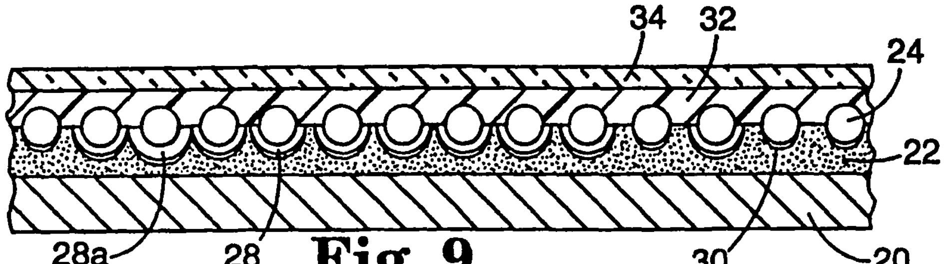

Fig 9

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/10736

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G02B5/128

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 203 752 (3M CO.) 3 December 1986 see column 10, line 30 - line 48; figure 3	1-8
X	EP,A,0 215 672 (3M CO.) 25 March 1987 see column 7, line 25 - line 58; figure 2	1-8
A	EP,A,0 170 518 (3M CO.) 5 February 1986 see the whole document	1-8
A	DE,A,21 24 414 (INT. COSMOS TRADE EST.) 30 November 1972 see the whole document	1-8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 November 1996	27. 11. 96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Sarneel, A

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat Application No
PCT/US 96/10736

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-203752	03-12-86	US-A-	4691993	08-09-87
		US-A-	4688894	25-08-87
		AU-B-	589173	05-10-89
		AU-A-	5654586	20-11-86
		CA-A-	1250952	07-03-89
		DE-A-	3686293	10-09-92
		JP-A-	61261701	19-11-86
		KR-B-	9408669	24-09-94
		CA-A-	1263264	28-11-89
EP-A-215672	25-03-87	CA-A-	1273512	04-09-90
		DE-A-	3682468	19-12-91
		JP-B-	8012282	07-02-96
		JP-A-	62066203	25-03-87
		KR-B-	9503435	12-04-95
		US-A-	4708920	24-11-87
EP-A-170518	05-02-86	US-A-	4650283	17-03-87
		AU-B-	568758	07-01-88
		AU-A-	4479185	06-02-86
		CA-A-	1273835	11-09-90
		DE-A-	3585812	14-05-92
		HK-A-	4693	29-01-93
		IE-B-	58653	03-11-93
		JP-C-	1854906	07-07-94
		JP-A-	61046976	07-03-86
DE-A-2124414	30-11-72	NONE		